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FORMATION OF THE BLACK CORE IN HIGH-SPEED FIRING OF FLOOR TILES

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The results of studying the black core in high-speed firing of floor tiles and the methods for its prevention are presented.

One of the peculiarities of high-speed firing of floor tiles is the emergence of the black core in the fired articles [2]. In order to elucidate the reasons for the formation of the black core, mixtures whose compositions are shown in Table 1 were investigated.

The physicochemical and ceramic properties and the chemical and mineral compositions of the components listed in Table 1 were studied earlier [2, 3].

To compare the masses under study in their susceptibility to formation of the black core, plates measuring 100 × 100 × 10 mm were made. The plates were fired in a laboratory furnace at different temperatures (Table 2) and the change in their color upon heating was observed.

The plates of all masses after quick-firing to a temperature of 1100°C exhibited a core which differed in color from the standard color of the mass in question: the black color was observed in the clay component of gravitation tails and in the combination of the gravitation tails clay component and the Zhana-Daurskoe clay; the gray color was observed in the white-burning Zhana-Daurskoe clay.

At the early phases of burning at temperatures of 800 – 1000°C, perceptible modification of color was observed only in tiles made of mixtures 1 and 3. Tiles made of mixture 2 at temperatures of 800 – 1000°C exhibited uniform color across their entire thickness.

To evaluate the data in Table 2, it is necessary to study the main processes which take place in firing ceramic mixtures containing organic impurities and iron oxides. The organic impurities consist either of various combustible particles in the form of scattered inclusions, or of humus (mulch) which is adsorbed by disperse particles of argillaceous material and occasionally enters in chemical reactions with them. Humus is the product of the decay of vegetative and animal organisms and the synthesis of new complex compounds formed as the result of biological and biochemical processes in soil.

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Organic impurities in heating are charred (mostly in the interior tile layers deprived of access to air oxygen) and decompose into volatile agents and carbonaceous residue whose combustion is impeded. The process is similar to dry distillation of fuel. According to several researchers, charring accompanied by the formation of carbonaceous residue occurs at temperature of 500 – 700°C [1]. In high-speed firing, the specified process is shifted toward higher temperatures.

As the carbonaceous residue is burned out, the following processes take place: oxygen diffusion through the tile layer, chemical reactions of combustion with the formation of carbon oxide inside the tile, carbon oxide diffusion toward the

TABLE 1

Component	Mass content, %, in mixture		
	1	2	3
Clay component of zircon-ilmenite ore gravitation tails	100	–	50
Zhana-Daurskoe clay	–	100	50

TABLE 2

Mixture	Normal color of tile	Heating duration, min	Temperature, °C	Width (mm) of stripes colored		
				gray	brown	black
1	Red	15	600	–	–	–
		20	800	–	–	–
		30	1000	–	3	–
		50	1100	–	4	6
2	White	15	600	–	–	–
		20	800	–	–	–
		30	1000	–	–	–
		50	1100	4	–	2
3	Light red	15	600	–	–	–
		20	800	–	–	–
		30	1000	4	–	–
		50	1100	6	–	4

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tile surface, and combustion of carbon oxide under the effect of ambient oxygen.

The burning rate of the carbonic residue is determined by the slowest process, i.e., diffusion of oxygen through the tile layer. Oxygen combines with carbon through the following reactions:

$$C + O_2 = CO_2 + 97{,}650 \text{ kcal}$$

$$2C + O_2 = 2CO + 58{,}860 \text{ kcal}$$

The existence of incandescent coal inside the tile with a deficit of oxygen results in reducing CO_2 to carbon monoxide according to the reaction

$$C + CO_2 = 2CO - 38{,}750 \text{ kcal}$$

The latter reaction within the low temperature region proceeds in the opposite direction with the formation of carbonic acid and free carbon. At temperatures above 1000°C, only CO is formed.

In firing ceramic articles, carbon combustion is complicated by the dehydration process which in accelerated firing conditions proceeds at temperatures above 500°C. In this context, the oxygen diffusion and, accordingly, the burning of the carbonaceous residue out are impeded. The amount of organic impurities in the samples fired in the steam-gas medium and in the water steam medium at temperatures of 750 – 850°C is 6 – 7 times higher than in the samples fired in an oxidizing medium [4].

If the carbon material in the course of sintering with participation of the liquid phase is insulated from air before it gets fully oxidized, at higher temperatures it will act as a reducing agent [4] (primarily in the form of CO, due to the reaction inside the tile $C = CO_2 \leftrightarrows 2CO$, which at higher temperatures is shifted to the right). In this case, the iron oxide in the iron-containing mixtures can be reduced by the following reactions:

$$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2;$$

$$Fe_3O_4 + CO = 3FeO + CO_2;$$

$$FeO + CO = Fe + CO_2.$$

Humus impurities are virtually totally absent in fully fired tiles (Table 3).

TABLE 3

Mixture	Content, %						
	in initial mixture			in tiles with a black core*		in tiles without a black core*	
	humus	Fe_2O_3	FeO	Fe_2O_3	FeO	Fe_2O_3	FeO
1	0.2	5.88	0.88	0.98	5.78	6.00	0.21
2	0.3	2.84	0.34	0.32	2.86	2.94	0.44
3	0.3	3.72	0.62	0.52	3.82	3.82	0.52

* Humus contained in trace quantities.

The considered tiles substantially differ in the content of Fe_2O_3 and FeO. In the tiles without the black core, Fe_2O_3 exceeds FeO, and in the tiles with the black core, the reverse relationship is true.

Fe_2O_3 is virtually nonexistent right inside the black core, since it is completely reduced to iron oxide (II) FeO, which is characterized by the black color [4]. Consequently, the blackness in the core of a completely fired tile is the result of Fe_2O_3 reduction to FeO, which agrees with the data in [4].

The modification of the main properties of the tiles based on the specified clays in the course of the black core formation can be divided into three phases: temperatures up to 600°C, when the tile color is uniform across the entire thickness, and the content of humus and iron oxide does not vary compared to the initial mixture; 600 – 800°C, when a black core begins to be formed, whereas the humus and iron oxide content remains constant, compared to the initial level; and above 1000°C, when the black core exists, the humus content decreases, and the content of FeO sharply increases (at the expense of Fe_2O_3).

At the temperatures of 800 – 1000°C, the black core is determined by the presence of the carbonaceous residue resulting from charring of organic impurities and in the finally fired tiles by the presence of FeO reduced from FeO_3.

The black core is not observed in tiles made from the Zhana-Daurskoe clay at temperatures up to 1000°C. However, this fact does not indicate the absence of charring of organic impurities in the tiles made of such clay. Charring does take place, but due to the insignificant content of humus (0.3%), the formation of the carbonaceous residue does not perceptibly modify the core color against the overall light red background of the tiles. The core in these tiles at temperatures up to 1000°C has a reddish tint instead of the usual light hues.

In choosing the heating conditions, it is necessary to take into account the burning out of carbon and completion of dehydration before the start of shrinkage. It should be noted that the black core did not appear in the completely fired tiles of mixtures 1 – 3 after 3 h holding at the temperature of 600°C. These mixtures are characterized by an insignificant humus content (0.2 – 0.3%), and 3-h holding at the temperature of 600°C provides for complete burning out of carbon in spite of the increased FeO_3 content in these mixtures. This points to the fact that the main cause for reducing iron oxide (III) to iron oxide (II) and, accordingly, for the presence of the black core in completely fired tiles is the nonburned out carbon.

The role of the reducing medium is also corroborated by the data on the formation of surface blackness in accelerated firing of floor tiles in an industrial roller furnace [4]. With the availability of CO in the firing area, the tiles have two zones of blackness: in the core and on the surface, and the zone whose color is typical of the given mixture is located between the black layers. The oxygen in the interspace between the core and the surface was completely burned before the tile arrived at the firing area. Moreover, this zone is pro-

tected by the tile surface layer from the effect of the CO gas medium, and blackness does not emerge in it [4].

The formation of the black core can be completely eliminated through holding the article for a certain time at a temperature of 800 – 950°C. As the temperature increases within the specified interval, the duration of holding decreases: for example, at a temperature of 800°C, the required holding period for tiles made of Zhana-Daurskoe clay is 20 min, and at 950°C, the holding duration is 10 min; for tiles made of gravitation tails clay components the holding duration is 15 and 8 min, respectively.

The intense shrinkage of tiles begins at temperatures above 950°C, which impedes the diffusion of oxygen and charring of the carbonaceous residue. Moreover, the process of iron reduction at these temperatures is significantly accelerated [1]. Consequently, it is inadvisable to hold an article at temperatures over 950°C for the purpose of burning out the carbon.

The presence of nonburned out carbon in the tiles during sintering can produce not only black cores but also such defects as swelling and cracks. These defects are especially typical of mixtures with an increased humus content.

In the present study, feldspar concentrate [5] was tested for the purpose of studying the effect of grog additives on black core formation.

It was established that by using 30 – 40% feldspar concentrate in tiles it is possible to prevent the formation of the black core without significantly extending the holding duration at temperatures of 800 – 950°C.

Tiles made of nonplastic materials exhibit enhanced gas permeability, thus providing oxygen diffusion which, in turn, promotes burning out of the carbonaceous residue and, consequently, eliminates the possibility of black core formation.

Thus to prevent origination of black cores, nonplastic masses should be used. Special attention should be paid to the adequate duration of the exposition within the temperature range of 800 – 950°C.

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